

Synthesis and characterization of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.2}\text{Ti}_{0.3}\text{O}_3$ Anodes for SOFCs

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Abstract. $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.2}\text{Ti}_{0.3}\text{O}_3$ has been synthesized in solid state reaction method and tested as a potential anode material for solid oxide fuel cells. Rietveld refinement of X-ray powder diffraction data of the composition using Fullprof software shows that the materials crystallize in the rhombohedral symmetry in the R-3C space group. The cell parameters are: $a = b = 5.5143(4) \text{ \AA}$, $c = 13.452(1) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\delta = 120^\circ$. Addition of titanium to the B-site of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ yields a total conductivity of 1.96 Scm^{-1} in air at 800°C with activation energy of 1.02 eV .

1. Introduction

Ni-YSZ cermet is the state of the art anode material for zirconia-based solid oxide fuel cells (SOFCs). However, this material suffers some drawbacks such as carbon deposition under hydrocarbon feed and poor redox cycling [1]. Recently, mixed conducting perovskite oxides such as the lanthanum and strontium titanates or lanthanum chromites, has been given attention [2-3]. The lanthanum and strontium chromo-manganite $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ were reported to be a promising anode material to replace Ni-YSZ cermet [3] and it shows good performances as a catalytic material for hydrogen and methane oxidation and redox stability in low steam to hydrocarbon ratios. Nevertheless, LSCM presents a low conductivity in air and in reducing conditions [4], and oxygen diffusion as well as surface exchange properties of LSCM [5] are lower than in other perovskites [6]. Although LSCM represents a promising anode material for SOFCs, various studies were done on LSCM based composites with yttria stabilized zirconia [7], gadolinia doped ceria [8] or metal catalyst [9,10] to improve anodic performance.

Adding dopants of transition metal elements enhances the properties of the anodes. The effects of the content and the nature of the dopant at A- or B- sites of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ solid solutions on electric and electrocatalytic properties have been evaluated [11-17] to assess the potential of these oxides as SOFC anodes. For instance, 10% of cerium substituted on the A-sites of LSCM was found to enhance the electrochemical performance without additional microstructural modification and without any change of the electrical conductivity in a reducing atmosphere [18]. Knowing the chemical flexibility in perovskite structure, titanium can be partially or totally substituted for chromium in LSCM, in order to study the effect of the material basicity on its overall performance.

In this study, we have prepared and characterized a new series of materials where Cr was substituted by Ti in $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$. Material was prepared by solid state sintering and characterized by using X-ray diffraction, four-probe conductivity and density measurements. The characteristics were found to be suitable to use this material as anode for solid oxide fuel cells.



2. Experimental

Powders of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_3$ were synthesized by the solid state sintering method. A total of 15.311 g of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_3$ was made by adding the following powders: 8.103 g of La_2O_3 (Merck Aldrich, 99.9%), 1.718 g of SrO (Merck Aldrich, 99.9%), 2.897 g of MnO_2 (China, 99.9%), 1.588 g of TiO_2 (Merck Aldrich, 99.9%) and 1.005 g of Cr_2O_3 (Merck Aldrich, 99.9%) as according to the stoichiometry. Powders were mixed with ethyl alcohol and ball milled overnight. The slurry was then put into an oven overnight at 100 °C to evaporate the solvent and the powder obtained was crushed with an agate pestle and mortar. About 2.0 g of the powder was pressed with a Kennedy hydraulic press at 3 tonnes in 20 mm radius die to make a pellet. The pellets were sintered at 1200 °C first by using a Nabertherm furnace. The pellets were again crushed and powders pelletized using the same condition and sintered at 1500 °C. In this paper, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_3$ will be identified as LSCMT.

The phase purity and crystal parameter were examined at room temperature by using a Shimadzu 7000 X-ray diffractometer using $\text{CuK}\alpha_1$ wavelength $\lambda = 0.15406$ nm at 40 kV and 30 mA and a scan speed of 1.0 deg/min. The experiment data were refined by a Rietveld method using the Fullprof [19] program. Winplotr which is available within the suit was used for powder diffraction data viewing and processing, peak profiling and indexing.

Resistance and conductivity was measured by a homemade DC four-probe setup in air over the temperature range of 100 °C to 800 °C. Ag wire and Ag paste were used to make the four probe. The electrical resistivity (ρ) was calculated by

$$\rho = RS/L \quad (1)$$

where S is the cross-sectional area and L is the length of the measured section. The conductivity (σ) was obtained by the reciprocal of the resistivity.

The pellets densities were measured by the Archimedes' method. The measured densities were compared with the theoretical densities using the relation

$$\rho_{\text{th}} = \frac{\text{molecular weight of compound}}{N_a \cdot \frac{\sqrt{3}}{2} a^2 \cdot c} \quad (2)$$

where N_a is the Avogadro constant, a, and c, are the lattice parameters for the sample.

3. Results and discussion

3.1. Structural analysis

The room temperature XRD powder patterns were indexed to know the single phase nature of the samples and to find the symmetry and cell parameters. Fig. 1 shows the X-ray powder diffraction patterns with the Rietveld refinement profile on the LSCMT sample. Unit cell parameters are related to the ideal cubic perovskite as $a \approx b \approx \sqrt{2}a_p$, $c \approx 4a_p$ ($z = 4$) where a_p is the cell parameter of the basic cubic perovskite $a_p \approx 3.91\text{\AA}$. Figure 2 shows the schematic three-dimensional view of the compounds. Structure parameters, interatomic distances and R-factors are obtained from the Rietveld analyses. Table 1 shows the cell parameters was found to be $a = b = 5.5143(4)\text{\AA}$, $c = 13.452(1)\text{\AA}$ for LSCMT; cell volume, $v = 354.25(5)\text{\AA}^3$; oxygen occupancy = 97.5%; oxygen position in 18e (0.460, 0, 0.25). This is close to the cell parameter of LSCM and Ce-LSCM as reported by Tao et al.[2] and Lay

et al.[18] respectively. The refinement converge in a good R-factors; $R_p = 9.91\%$ and $R_{wp} = 14.7\%$ and $\chi^2 = 0.86$. The high values of R-factors are due to the bad statistics of data. Since χ^2 value is very reasonable and profile matching is good, we accept the refinement.

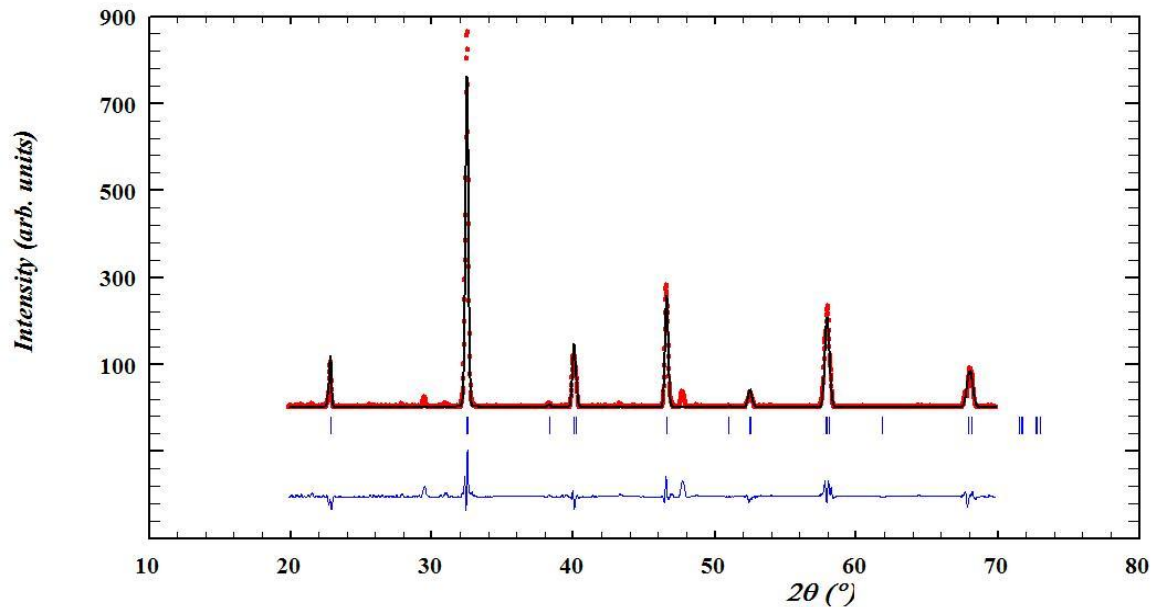


Figure 1. Observed line(red) and calculated(black) XRD intensity profiles for LSCMT. The blue line indicates the difference plot $I_{\text{obs}} - I_{\text{calc}}$

Table 1. Refined cell parameters for $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$, $\text{La}_{0.65}\text{Ce}_{0.1}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ and $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{3-\delta}$

	LSCM[2]	Ce-LSCM[18]	Ti-LSCM(this work)
a (Å)	5.5144	5.4973	5.5143
c (Å)	13.401	13.321	13.452
V (Å ³)	352.92	348.65	354.25

As shown in figure 2, the B-site cations (Mn/Cr/Ti) are surrounded by regular octahedra of oxygen. These octahedra are linked together in a corner sharing three dimensional frameworks, while La/Sr ions occupy 12-coordinated A-site between these octahedra.

The Mn/Cr/Ti- O_6 octahedra are elongated along the c -axis. The crystal structure was distorted due to relative size differences of the A and B cations, which force the (Mn/Cr/Ti) O_6 octahedra to tilt in order to optimize the La/Sr-O bond distances. The tilting of the octahedra can also be realized looking the Goldschmidt tolerance factor (t) as shown in (3),

$$t = \frac{(Ra+Ro)}{\sqrt{2}(Rb+Ro)} \quad (3)$$

where R_a , R_b and R_o are the ionic radii of A-site, B-site and oxygen. When $t < 1$, the octahedra are tilted. Based on the ionic radii of La^{3+} ($r = 1.36$ Å), Sr^{2+} ($r = 1.44$ Å), Mn^{3+} ($r = 0.645$ Å),

Cr^{3+} ($r = 0.615 \text{ \AA}$), Ti^{3+} ($r = 0.67 \text{ \AA}$) and O^{2-} ($r = 1.40 \text{ \AA}$) [20] in appropriate coordination number, the tolerance factor was calculated to be $t = 0.965$.

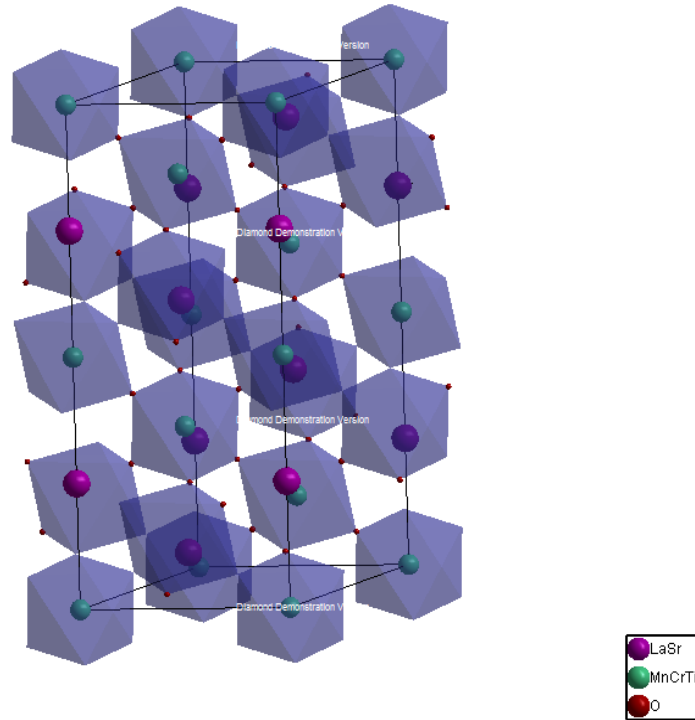


Figure 2. Schematic 3D structure of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{3-\delta}$.

3.2 Electrical conductivity analysis

Electrical conductivity is an important parameter for SOFC anode since a sufficiently high electronic conductivity is required to provide transfer of generated charge. The minimum electrical conductivity of 1 S cm^{-1} value was proposed [1]. The Arrhenius plot of LSCMT is shown in figure 3. The maximum electrical conductivity in air 1.96 S cm^{-1} at 800°C . The activation energy is 1.02 eV .

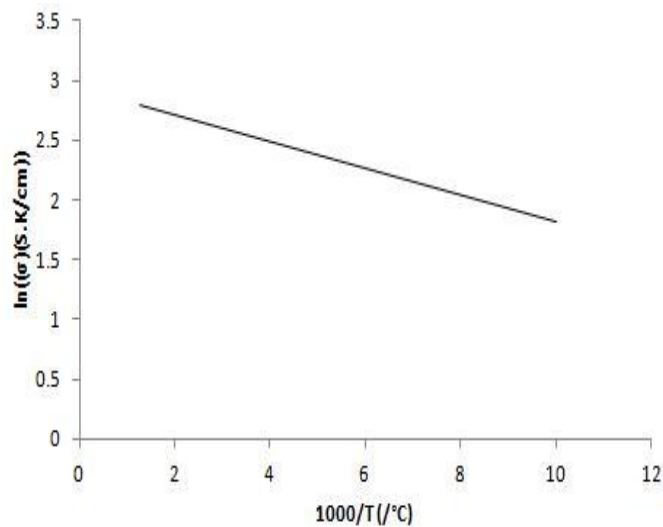


Figure 3. Electrical conductivity of LSCMT in air

3.3 Density analysis

The theoretical density is 6.44 g cm^{-3} . The actual density is found to be 6.00 g cm^{-3} . Therefore the porosity is 6.83%. This indicates that the material is suitable to be an anode for the SOFC as higher porosity is required to have a larger surface area for the anode to be in contact with hydrogen fuel during operation.

4. Conclusion

A perovskite $\text{La}_{0.75}\text{Sr}_{0.25}\text{Mn}_{0.5}\text{Cr}_{0.2}\text{Ti}_{0.3}\text{O}_3$ has been synthesized by a solid state reaction. The XRD analysis results indicate that a pure perovskite phase can be obtained in air for 8 hours and 10 hours subsequently after treatment. The crystal structure has been refined at room temperature and shows a rhombohedral symmetry in the R-3C space group. The Ti-doped material has a high electrical conductivity and low activation energy making it suitable as an anode for the SOFC.

Acknowledgments

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References

- [1] Atkinson A, Barnett S, Gorte R J, Irvine J T S, McEvoy A J, Mogensen M, Singhal S V and Voh J 2004 *Nat. Mater.* **3** 17-27
- [2] Tao S and Irvine J T S 2004 *J. Electrochem. Soc.* **151** A252-59
- [3] Canales-Vasquez J, Tao S W and Irvine J T S 2003 *Solid state ionics* **159** 159-165
- [4] Plint S M, Connor P A, Tao S and Irvine J T S 2006 *Solid state ionics* **177** 2005-08
- [5] Raj E S, Kilner J A and Irvine J T S 2006 *Solid state ionics* **177** 1747-52
- [6] Wang L, Merkle R, Maier J, Acarturk T and Starke U 2009 *Appl. Phys. Lett.* **94**
- [7] Kim G, Corre G, Irvine J T S, Vohs J M and Gorte R J 2008 *Electrochem. Solid-State Lett.* **11** B16-19
- [8] Chen X J, Liu Q L, Khor K A and Chan S H 2007 *J. Power Sources* **165** 34-40
- [9] Zhu X, Lü Z, Wei B, Zhang Y, Liu M, Huang X and Su W 2010 *J. Electrochem. Soc.* **157** B691-96
- [10] Barison S, Fabrizio M, Mortalo C, Antonucci P L, Modafferi V and Gerbasi R 2010 *Solid State Ionics* **181** 285-291
- [11] Ghosh A, Azad A K and Irvine J T S 2011 *ECS Transac.* **35** 1337-43
- [12] Azad A K, Hakem A and Petra P I 2015 *AIP Conference proceedings*, **1660** 070069.
- [13] Azad A K and Irvine J T S 2011 *Solid State Ionics* **192** 225-228
- [14] Basheer F, Ming L C, Petra P I and Azad A K 2015 *ECS Transactions* **68(1)** 1481-88
- [15] Van Den Bossche M and McIntosh S 2010 *Chem. Mater.* **22** 5856-65
- [16] Fonseca F C, Mucillo E N S, Mucillo R and De Florio D Z 2008 *J. Electrochem. Soc.* **155** B483-87
- [17] Jeong J, Azad A K, Schlegl H, Kim B, Baek B W, Kim K, Kang H and Kim J H 2015 *Solid State Chem.* **226** 154-163
- [18] Lay E, Gauthier G, Rosini S, Savaniu C and Irvine J T S 2008 *Solid State Ionics* **179** 1562-66
- [19] Rodriguez-Carvajal J 1993 *Phys. B Condens. Matter*, **192** 55
- [20] Shannon R D 1976 *Acta Crystallogr.* **A32** 751